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UNPUBLISHED PRELIMINARY DATA

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The major research activity of this project is concerned with the fundamental acts of cross-linking polymers and the determination of the manner in which the efficiency of cross-linking and the properties of the resultant isotropic network depend on the state of the polymer at the time the crosslinks are introduced. Major attention at present is being given to polyethylene, and crosslinks are introduced into this polymer by means of high energy ionizing radiation. Specifically, x-rays from a three m. e. v. Van der Graaf are being used for this purpose.

In the previous status report (September 1, 1963) the results obtained for unfractionated linear polyethylene were discussed. In summary, the completely amorphous polymer and the highly crystalline polymer were irradiated at 130°C, and it was found that crosslinking was much more efficient in the highly crystalline polymer at this temperature. This type of study has now been extended to molecular weight fractions of linear polyethylene so that the analysis of gel formation and the partitioning between sol and gel can be made without the complexities of the initial molecular weight distribution. Fractions encompassing the molecular weight range from 1.1×10^5 to 1.0×10^6 have been studied. The crosslinking process in the amorphous state at 130°C follows theoretical expectations. The gel-point is inversely proportional to the molecular weight and with the exception of the highest molecular weight fraction, the partitioning between sol and gel also follows the dictates of theory. The deviations observed for the highest molecular weight fraction can be attributed to polydispersity. Each of the fractions were also isothermally crystallized in the bulk to high levels of crystallinity at 130°C and irradiated at the same temperature after the

the crystallization process was completed. The efficiency of crosslinking the crystalline fractions was approximately twice that of the completely amorphous polymers over the entire range of sol-gel partitioning. These results and their interpretation have been described in detail in a paper accepted for publication in the Journal of Polymer Science.

The study of the crosslinking process of the highly crystalline polymers, crystallized in bulk, has now been extended to lower temperatures of irradiation. As the temperature is lowered the relatively high crosslinking efficiency is maintained until about 90°C. Below this temperature, it is found that the crosslinking process becomes highly inefficient and at room temperature extremely high radiation doses are required in order to introduce any significant number of crosslinks into a highly crystalline polyethylene fraction. These results are being summarized in a manuscript that is being prepared at present. It is clear from these results that the crosslinking efficiency depends not only on the state of the system, but also on the temperature at which the crosslinks are introduced. Preliminary experiments indicate that the same type of temperature coefficient of crosslinking is observed in highly oriented crystalline fibers as well as in single crystals prepared from dilute solutions. In the latter case, however, complications in interpretation exist, since morphological changes occur in the crystals with increasing temperature.

The drastic and sudden change that occurs in the vicinity of 90°C in the crosslinking efficiency of the crystalline region is indicative of some type of molecular motion or transition in the crystalline state of polyethylene.

This possibility is being investigated further by means of very sensitive dilatometric studies as well as by nuclear magnetic resonance techniques.

Equilibrium swelling measurements of the amorphous polymers have been made on the specimens crosslinked at different temperatures in the different states. The data is being analyzed at present with emphasis being placed on the differences in elastic properties of networks formed at the same sol-gel ratio.